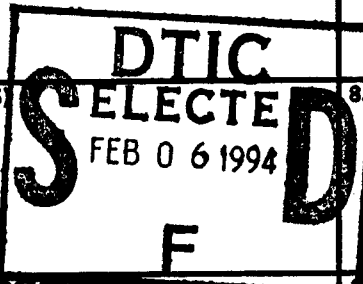# REPORT DOCUMENTATION PAGE

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Transitions in Liquid Crystals Initiated with Circularly Polarized Light

Final Report

Gary B. Schuster

September, 1994

U. S. Army Research Office

ARO 111-94

University of Illinois

PROJECT SUMMARY

Transitions in Liquid Crystals Initiated with Circularly Polarized Light

The fundamental goal of this research is the discovery of new means to control the physical and optical properties of liquid crystals with light. In work on this project we focused on the development of chiroptical triggers designed to induce a reversible nematic to cholesteric transition in a liquid crystal under the influence of circularly polarized light. Three classes of systems were investigated - biaryl chromophores, axially symmetric benzylidene cyclohexanes, and chiral cycloheptatrienes. None of these compounds meet all of the requirements for a chiroptical trigger, but the knowledge gained enables a clearer definition of the properties a successful trigger must posses.

(II) SUMMARY OF RESEARCH ACCOMPLISHMENTS

A. Introduction. The primary objective of the research supported by this grant has been the discovery of a new type of liquid crystal-based optical switch.[1] It is known that irradiation of certain chiral compounds with circularly polarized light (cpl) leads to their partial photoresolution by enrichment of one enantiomer at a photostationary state (pss).[2] The amount of this enrichment ($[\gamma]_{PSS}$) is equal to $\Delta\varepsilon/2\varepsilon$, where $\Delta\varepsilon$ is the difference in extinction coefficients of the enantiomers with cpl, and ε is the average extinction coefficient. It has previously been demonstrated that addition of an enantiomerically enriched mixture of a chiral compound to a nematic liquid crystal material

Scheme 1. Concept of Chiroptical Liquid Crystal Switch

Racemic Trigger	CPL	Optically Active Trigger
Nematic Liquid Crystal	Un-Polarized h	Cholesteric Liquid Crystal
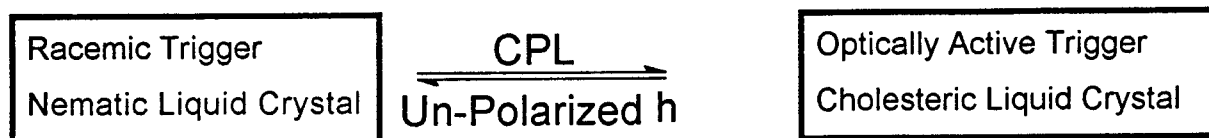
(for example) induces a helical pitch in the phase (i.e., forms a cholesteric liquid crystal).[3] The helical pitch of this phase can be sensed optically either by the rotation or reflection of plane polarized probe light. Of course, the enantiomerically enriched compound can be converted back to the racemic mixture by irradiation with un-polarized light. Formation of the racemate will result in regeneration of the nematic phase of the liquid crystal. Thus in the proposed chiroptical switch, information is encoded (simply as ON and OFF, for example) in circularly polarized light which is absorbed by a chiral "trigger" molecule dissolved in a nematic liquid crystal. This light initiates a photochemical reaction that results in the enantiomeric enrichment of the trigger. The enriched trigger induces formation of a twisted liquid crystal phase that can be sensed with probe light at a non-absorbed wavelength. Finally, irradiation of the enantiomerically enriched trigger with un-polarized light reforms the racemic mixture and converts the cholesteric liquid crystal back to the nematic phase. These concepts are outlined in Scheme 1. Clearly, finding suitable trigger molecules is the key to the discovery of a chiroptical switch of the sort described. Our work on this project has been focused on this task. We have learned that an effective trigger molecule must simultaneously satisfy seven key requirements:

1. The trigger must undergo an efficient photochemical reaction that interconverts its enantiomers. This prerequisite is quantified by measurement of the quantum yield for racemization (Φ_{rac}) of possible triggers. If Φ_{rac} is small, the formation of the

enantiomerically enriched photostationary state will be very slow because the rate expression for photoresolution depends exponentially on this quantity.[4]

2. The twisting power (β_M) of the enriched dopant must be large.[5] Since it is difficult to obtain very high enantiomeric enrichments by photoresolution (see below), the trigger molecules must be designed to take maximum advantage of a small enrichment.

3. The trigger must be photostable. That is, its irradiation cannot result in any reaction other than the interconversion of its enantiomers. This is particularly crucial if Φ_{rac} is small since, in this case, attainment of the photostationary state requires that each trigger molecule be excited many times.

4. The trigger must absorb at a wavelength where the liquid crystal host is transparent. Fortunately, this is not a difficult criterion to meet since saturated hydrocarbon mesogens are known and, by definition, the triggers we seek must have a chromophore.

5. The enantiomers of the trigger must be thermally stable. Thermal racemization of the trigger will spontaneously destroy the enantiomeric excess. Since there are compounds that exhibit liquid crystalline phases at room temperature, we seek compounds that have half-lives for thermal racemization of at least one hour at room temperature.

6. The trigger must be soluble in the liquid crystal phase. At one extreme, the trigger molecule itself forms the phase (a photoresolvable mesogen). This condition provides one limit to sensitivity to light since it will require the smallest values of β_M and $[\gamma]_{PSS}$. However, it is difficult to predict what compounds will form suitable liquid crystalline phases.

7. The $[\gamma]_{PSS}$ resulting from photoresolution by irradiation with circularly polarized light must be great enough to induce a detectable twisted phase. We have determined empirically that the maximum pitch (p) that can be sensed easily by optical microscopy is ca. 100 μm.[6] At low additive concentration $p = 1/\beta_M C\gamma$, where C is the mole fraction of the dopant in solution. Thus the minimum acceptable value for $[\gamma]_{PSS}$ is 5×10^{-3} calculated with $\beta_M \approx 20$ μm^{-1} and with $C \approx 0.1$.

The discovery of trigger molecules that satisfy these requirements is a more difficult task than was imagined at the outset of this work. The most demanding requirement is finding compounds that give satisfactory values of $[\gamma]_{PSS}$. It is possible to calculate this quantity from absorption and circular dichroism spectra. Of course, the measurement of $\Delta\epsilon$ requires synthesis and optical resolution of the potential triggers. This is a very time-consuming task. Alternatively, $\Delta\epsilon$ can be estimated by theoretical molecular orbital methods.[7]

The research completed during the present grant period did not produce a trigger molecule that satisfies all of the requirements listed above. However, we have made significant progress toward that goal, and the knowledge we gained has allowed us to broaden the search for photochemical triggers to compounds beyond those that rely on induction of an enantiomeric excess with circularly polarized light.

B. *Bis*-Binaphthyl Based Triggers. Our first attempt to prepare a chiroptical trigger was based on the known optical and photochemical properties of the 1,1'-binaphthyl system. The compounds we investigated are shown in Chart 1. This work has been described in detail (*J. Phys. Chem.*, 1992, 96, 3063); the key findings are summarized here.

Some time ago Irie,[8] showed that 1,1'-binaphthyl undergoes photoracemization in its triplet state. However, the unimolecular Φ_{rac} for 1,1'-binaphthyl is low, and it spontaneously racemizes near room temperature. To circumvent these problems, we chose ethano-bridged binaphthyl **1**, acetal **2**, and the diethers **3** as possible chiroptical triggers. These compounds seemed like promising candidates for several reasons. First, several chiral binaphthyl-group containing compounds had been examined as dopants in nematic liquid crystals and they were found to have relatively large β_M values.[5] Second, the synthesis of **1** in optically active form had been reported in the literature,[9] and compounds **2** and **3** could be readily prepared from commercially available, optically active 1,1'-*bis*(binaphth-2-ol). Further, Tétreau and co-workers studied the photochemistry of **2** and found that it photoracemizes with $\Phi_{rac} \approx 0.5$ (it should be noted that $\Phi_{rac} = 0.5$ is the theoretical limit for a unimolecular photoracemization).[10] Finally, since these binaphthyl derivatives have intrinsically chiral chromophores, we expected that $[\gamma]_{PSS}$ would be sufficiently large to induce a detectable pitch in a nematic liquid crystal phase. On the basis of these expectations, we synthesized compounds **1**, **2**, and **3** and examined their photochemical and materials properties.

Chart 1. Potential Bi-Naphthyl Based Triggers
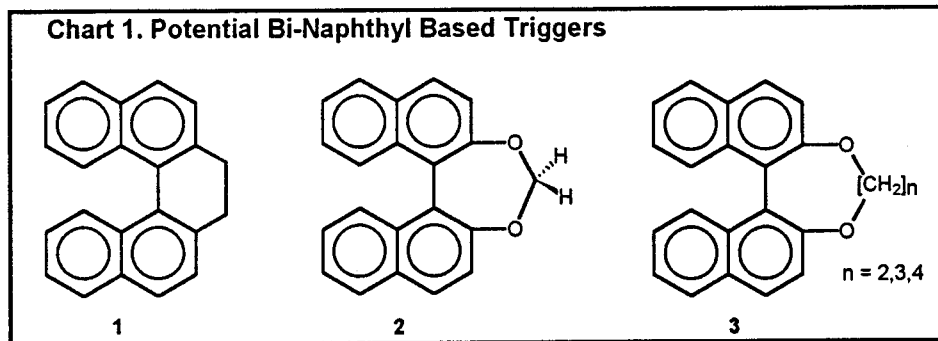
Analysis of the circular dichroism and UV spectra of ethano-bridged naphthalene **1** reveals that $[\gamma]_{PSS}$ is 12.5 x10^{-3}. This value clearly is large enough to induce a detectable helical pitch in a nematic liquid crystal phase (p $\approx$ 40 μm at the pss). However, we discovered that photolysis of optically active **1** gives unacceptably slow racemization. For example, irradiation of a 4.6 x 10^{-5} M cyclohexane solution of **1** for more than 4 hr results in less than 10% racemization (with significant accompanying photodegradation). At the time these experiments were completed, the inefficient racemization of **1** was thought to be a consequence of its high fluorescence efficiency since deactivation of the excited singlet will prevent the formation of the photoracemizing triplet state. Results from further study of binaphthyl-based systems indicate that the high fluorescence efficiency of **1** is only part of the explanation for its low Φ_{rac}. The activation energy for racemization of 1,1'-binaphthyls in their excited triplet states is extraordinarily sensitive to substituents.

Since Φ_{rac} of **2** was known to be large, we reasoned that its use as a chiroptical trigger would avoid the problem encountered with **1**. We confirmed Φ_{rac} for **2** - a cyclohexane solution is completely photoracemized in a few seconds of irradiation. But, analysis of the circular dichroism and UV spectra of **2** reveals that $[\gamma]_{PSS}$ is only 1 x 10^{-3} so the pitch that could be obtained in a doped nematic liquid crystal is 500 μm - a value beyond our detection limit.

These findings revealed an apparent dilemma: **1** has a satisfactory $[\gamma]_{PSS}$ but a Φ_{rac} that is too small. For **2** the situation is just reversed - Φ_{rac} is satisfactory but $[\gamma]_{PSS}$ is too small. We tried to resolve this problem by use of the 1,1'-binaphthyl ethers **3** as chiroptical

triggers. We hoped that Φ_{rac} and $[\gamma]_{PSS}$ would depend separately on the length of the alkyl chain that connects the binaphthyl groups. Indeed, both Φ_{rac} and $[\gamma]_{PSS}$ are sensitive to structure. Unfortunately though, as Φ_{rac} increases $[\gamma]_{PSS}$ decreases and, consequently, these compounds are not satisfactory chiroptical triggers.

We studied the photophysical and chemical dynamic properties of the 1,1'-binaphthyl based compounds **1**, **2**, and **3**. Time-resolved laser spectroscopy revealed efficient triplet formation (except for **1**), and long triplet lifetimes (ca. 10 μs) in all cases. The cause of the problem was finally revealed with the aid of molecular mechanics calculations of the thermal barrier to racemization and by consideration of the effect of the inter-ring dihedral angle (Θ_D) on $[\gamma]_{PSS}$. Simply put, when Θ_D is small, the activation barrier for racemization is low (the ground state energy is high), but $[\gamma]_{PSS}$ is small. When Θ_D is large, $[\gamma]_{PSS}$ is adequate, but Φ_{rac} is small because the activation barrier for racemization is high (the ground state energy is low). This finding indicates that 1,1'-binaphthyl compounds will not be satisfactory chiroptical triggers. Our search for a chiroptical trigger turned next to the investigation of 1,1'-biphenylenyl compounds.

C. Biphenylene Absorbers. Biphenylene is an unusual "aromatic" hydrocarbon with unusual spectroscopic properties.[11] Two facts of relevance for the development of a chiroptical trigger based on biphenylene are that its lowest energy optical transition is strongly forbidden (ε_{max} = 100 $M^{-1}cm^{-1}$), which should contribute to a large value of $[\gamma]_{PSS}$. And,

Chart 2. Potential Bis-Biphenylene Based Triggers

X = H, COCH₃, Br, OMe

4 **5, 6, 7, 8**

molecular mechanics calculations predict that the barrier to thermal racemization of 1,1'-biphenylenyl compounds should be significantly lower than for the corresponding naphthyl-containing systems (i.e., Φ_{rac} should not be so sensitive to Θ_D). We prepared the series of biphenylene - containing compounds shown in Chart 2 and studied their photochemical and photophysical properties.[12] The findings are summarized here and described in detail elsewhere (*J. Phys. Chem.* **1993**, *97*, 9299).
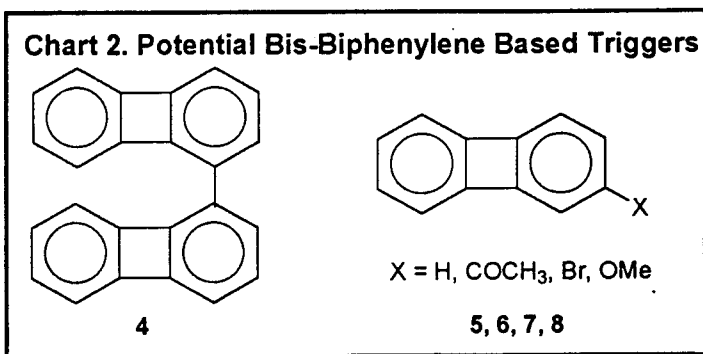
The key issue in the discovery of biphenylenyl-based compounds suitable for use as a chiroptical trigger is the intersystem crossing yield (Φ_{ISC}). The lifetime of excited singlet biphenylene is so short (ca. 240 ps) that photoracemization from this state is impossible. Consequently, to assure an acceptable Φ_{rac}, intersystem crossing to the triplet state must be efficient. For biphenylene itself (**5**), Φ_{ISC} is very small. We prepared compounds **6-8** to probe the effect of substituents expected to accelerate intersystem crossing on the biphenylene nucleus. *Bis*-biphenylene **4** was prepared to study Φ_{ISC} in a model close to potential chiroptical triggers.

The results were disappointing. Based on analogy with 2-bromonaphthalene and with 2-acetonaphthaone, we expected that the heavy atom effect of the bromine substituent in **7** and the nπ* states in the carbonyl group of **6** would accelerate intersystem crossing in these biphenylene derivatives.[13] They did not. We measured the singlet and triplet lifetimes by time-resolved absorption spectroscopy for **4 - 8** and found that these substituents accelerate non-radiative relaxation of the singlet states without significant enhancement of Φ_{ISC}. We attribute this surprising result to a reduction in symmetry of the substituted biphenylenes.

D. Benzylidene Cyclohexanes. Our next attempt to produce a chiroptical trigger was based on chiral, C_2-symmetric benzylidene cycloalkanes. A primary motivation for selection of this group was to overcome the low Φ_{rac} encountered with the biaryls. We hoped that Φ_{rac} for the benzylidene cycloalkanes would be uniformly large since racemization requires only the rotation about a carbon-carbon double bond in an excited electronic state. This reaction is analogous to the *cis* ⇔ *trans* photoisomerization of olefins, which has been extensively studied and is usually efficient for both singlet and triplet excited states.[14]

The major issue to be addressed in the benzylidene cycloalkane study was the magnitude of $[\gamma]_{PSS}$ that could be achieved in this system. In this regard we relied on chiral exciton coupling theory[15] to guide selection of the compounds for synthesis and examination. In brief, this theory predicts that two chromophores located in chiral positions with respect to each other are separated into two levels by Davydov splitting. The circular dichroism spectra of such molecules show opposite Cotton effects for absorption to these two levels. This interaction gives rise to a characteristic sigmoid circular dichroism feature known as the split Cotton band. The magnitude and the sign of the split Cotton band depend on the interchromophoric distance vector, the electric transition dipole moments of excitation, and the interaction energy between the two chromophoric groups. In general, the magnitude of $\Delta\varepsilon$ should increase directly with the spectral overlap of the two chromophores and inversely with the distance between them.

Chart 3 Potential Chiral Benzylidene Cycloalkane Based Triggers
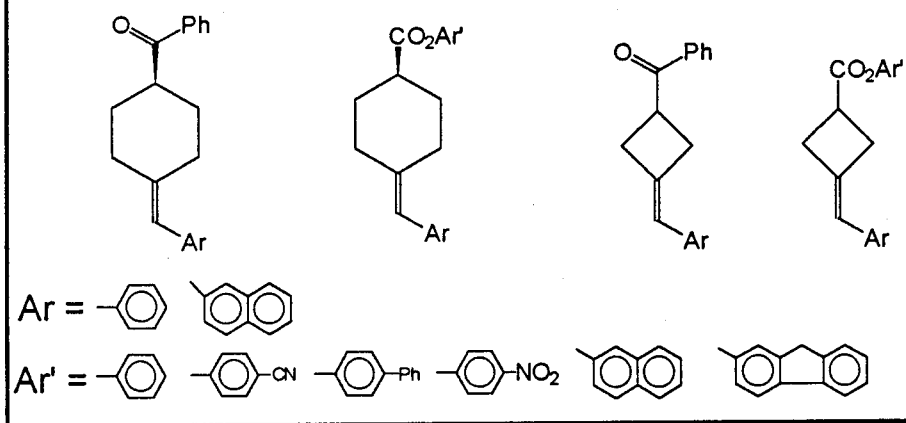
Our objective is to maximize $[\gamma]_{PSS}$ for photoresolvable compounds. To achieve this, the magnitude of $\Delta\varepsilon$ in a bichromophoric molecule must increase more than the extinction coefficient. This is precisely the prediction from chiral exciton coupling theory: $\Delta\varepsilon$ should increase approximately as the product of extinction coefficients of the individual chromophores, whereas the extinction coefficient of the bichromophoric compound should increase only as their sum. We prepared the series of compounds shown in Chart 3 to test this approach. The results are summarized here - the full details are reported elsewhere (*J. Org. Chem.* 1993, *58*, 100).

The compounds shown in Chart 3 can be divided into four classes: (*i*) six-membered ring esters; (*ii*) four-membered ring esters; (*iii*) six-membered ring phenyl ketones; and (*iv*) four-membered ring phenyl ketones. The chromophoric groups Ar and Ar' were selected to provide maximum spectral overlap, and the ring size was varied to control the interchromo-

phoric distance. The phenyl ketones were prepared to increase $[\gamma]_{PSS}$ by reducing the extinction coefficient for absorption in their $n\pi^*$ region.

The results from this study are encouraging. The optically active compounds were prepared in high yield and good enantiomeric purity by adaptation of the Hanessian chiral olefin synthesis.[16] The β_M values for the esters, determined by the droplet method[17] in K15 or ZLI-1167, ranged from 10 to 20 μm^{-1} (for the ketones β_M ranges from 5 to 10 μm^{-1}). The Φ_{rac} is high - photoracemization is complete in a few seconds for all of the compounds studied. And, critically, chiral exciton coupling theory correctly predicts the trend observed in $[\gamma]_{PSS}$. The magnitude of $[\gamma]_{PSS}$ increases more than a hundred-fold as the spectral overlap is increased and the interchromophoric distance vector is reduced. The maximum value of $[\gamma]_{PSS}$ observed is 5×10^{-3} for the four-membered ring phenyl ketones. Unfortunately, these compounds are photochemically unstable - irradiation causes rupture of the four-membered ring and this leads to the rapid destruction of the compound. The six-membered ring ketones and esters are stable photochemically, but their $[\gamma]_{PSS}$ values are about five times smaller than for the four-membered rings. We attempted to overcome this difficulty by preparing six-membered ring compounds that are themselves mesogens. This has the effect of raising the trigger concentration (C) from ca. 0.1 to 1.0 and should overcome the reduced value of $[\gamma]_{PSS}$.
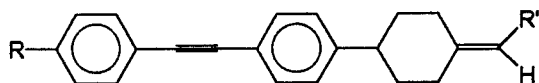
E. Photoresolvable Mesogens.

The search for benzylidene cyclohexane based photoresolvable mesogens is outlined here - the full details are described elsewhere (*J. Org. Chem.* **1994**, *59*, xxxx). Since we seek photoresolvable compounds that will form liquid crystalline phases, we are guided by the observation that many such compounds have semi-rigid, rod-like shapes. In particular, Miyazaki[18] reported that cyclohexyl-substituted

Chart 4. Potential Photoresolvable Mesogens

R = H; R' = Ph
R = H; R' = p-PhCN
R = H; R' = p-Ph-Ph
R = H; R' = 2-Naphthyl
R = C_5H_{11}; R' = Ph

R = C_5H_{11}; R' = p-PhCN
R = C_5H_{11}; R' = p-Ph-Ph
R = C_6H_{13}; R' = p-PhCN
R = H; R' = p-MeCOPh
R = H; R' = p-PhCOPh

diphenylacetylenes form nematic liquid crystals with a wide mesogenic range. The diphenylacetylene group thus seemed to be a good choice for one of the chromophoric units in a photoresolvable mesogen since its absorption spectrum shows a strong band at ca. 280 nm, ($\varepsilon = 2.84 \times 10^4$ $M^{-1}cm^{-1}$). We selected the β,β-dialkylstyrene group as the second chromophore since 1-benzylidene-4-substituted cyclohexanes are chiral and this photoresolvable functional group shows an absorption at 245 nm with $\varepsilon \approx 10^4$ $M^{-1}cm^{-1}$. Thus the spectral properties of these two chromophores appear to satisfy the requirements of chiral exciton coupling theory. Moreover, it seemed likely that suitable liquid crystalline chiral 1-benzylidene-4-[p-(alkyl)phenylethynyl]phenylcyclohexanes could be found. We prepared the series of such compounds shown in Chart 4, measured their spectral properties, examined their photochemistry, and tested their liquid crystalline behavior.

The synthesis of these compounds is triply convergent and again makes use of the Hanessian olefination to prepare the optically active form. The liquid crystalline properties of these compounds were examined to assess their suitability to function as photoresolvable mesogens. Photomicrographs of the racemic compounds show fan-shaped textures characteristic of a smectic phase.[19] Further heating leads to clearing without visible formation of a nematic phase. The optically active compounds also form textures that resemble smectic phases with strongly double refracting lancets. The β_M values for the optically active mesogens were determined in ZLI-1167 by application of the droplet method in a

glycerol suspension. Microscopic inspection of droplets containing ca. 3.5% of the dopants gives $\beta_M \approx 25 \ \mu m^{-1}$.

As expected, the electronic absorption spectra of these compounds appear as the sum of two components: the absorption of the benzylidene cyclohexane unit underlies the absorptions of the diphenylacetylene group. The circular dichroism spectra of these compounds have split Cotton bands as predicted from chiral exciton coupling theory. The extreme (a minimum for the (-) enantiomer) in the CD spectrum of the phenyl ketone substituted example occurs at 310 nm and gives $[\gamma]_{PSS} = 7 \times 10^{-3}$ for absorption in the $n\pi^*$ region of the carbonyl chromophore. Photoresolution of this compound with circularly polarized light would yield a detectable pitch if it formed a nematic liquid crystal phase.
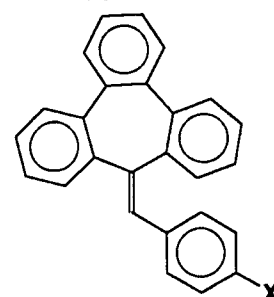
The results of the studies of the chiral benzylidene cycloalkanes were modestly encouraging but, ultimately, we decided that these compounds fell short of our goal. A complete optimization would require preparation of compounds which incorporate simultaneously the structure that gives the largest $[\gamma]_{PSS}$ and the greatest β_M value and, in its racemic form, have a nematic phase. We did not do this. If we assume that combination of these features in one compound would give a photoresolvable mesogen maintaining the best of both, then the minimum pitch that could be obtained is ca. 60 μm. This value is within the detectable range and, therefore, might function as a chiroptical trigger. However, this conclusion is based on a linear extrapolation of β_M from a 3.5% solution to a neat phase - which is uncertain. Since a decrease in β_M of only a factor of 2 would make the pitch undetectable, we chose not to proceed with the optimization.

F. Cyclohepatriene Based Triggers. Analysis of the problems encountered in the search for a suitable chiroptic trigger led us to consider systems that contain an inherently chiral chromophore (to give it a large $[\gamma]_{PSS}$) that is racemized by double bond isomerization (to give it a high Φ_{rac}). A careful search of the literature indicated that 1-benzylidene-tribenzocycloheptatrienes (see Chart 5) might satisfy these criteria.[20] The findings from this study are outlined here - the details are reported elsewhere (*J. Org. Chem.* **1993**, *58*, 4165.)

Chart 5. Potential Cycloheptatriene Triggers

X = H, Ph, CN, F, COCH$_3$

The syntheses of the optically active cycloheptatrienes made use, again, of the Hanessian olefination reaction. The absorption spectra of these compounds tail to ca. 330 nm, which is indicative of the extended π-electron conjugation. Experiments revealed that these compounds are photochemically stable, that they exhibit the hoped for large Φ_{rac} values, and that they have satisfactory β_M values (40 μm^{-1} in ZLI-1167 for X = Ph). Unfortunately, the $[\gamma]_{PSS}$ values that can be obtained in this system are only modest. The maximum value, when X= F, is 1×10^{-3} is - too small to pursue the development of a photoresolvable mesogen based on this chromophoric group.

G. Volume Holograms. The optical triggers we hope to discover may have application to devices. We have established a collaboration with Professor David Brady of the Department of Electrical and Computer Engineering at the University of Illinois to explore this possibility. Our first cooperative effort led to the discovery of a system for holographic storage in a near-IR sensitive photochromic medium. This work was recently published in *Optics Commun.*; the key findings are summarized here.

7

We seek to discover new dynamic holographic media with high sensitivity to near-IR light.[21] Our first attempt is based on the spirothiopyran class of photochromic compounds (see Chart 6.) Irradiation of the spirothiapyran with UV light converts it to the merocyanine form which absorbs in the near-IR region. Irradiation of the merocyanine with 780 nm light converts it back (in part) to the spirothiapyran.[22] The conversion of the merocyanine to spirothiapyran results in a large change in shape for this trigger molecule. We hope to use this shape change to modify the local order in a polymer (our first attempt), or in a liquid crystal medium (PROPOSED RESEARCH FOR THE NEXT GRANT PERIOD).

Chart 6. Near IR Sensitive Holographic Switch

Spirothiapyran   Merocyanine
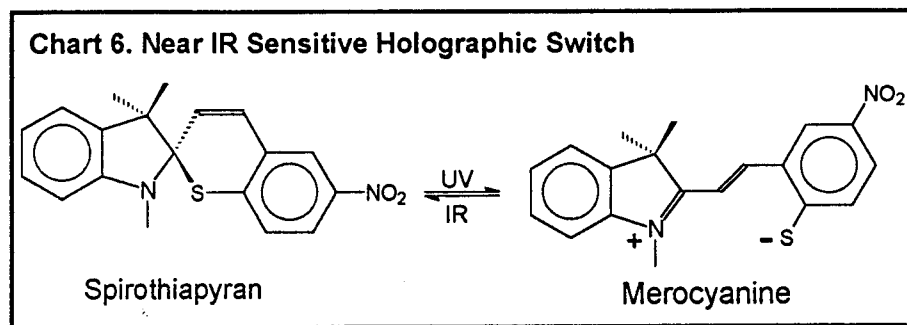
Our preliminary findings reveal that a holographic grating can be written with a diode laser in polymethylmethacrylate (PMMA) containing the merocyanine dye. This process is reversible but inefficient because there is only a small change in refractive index and a concomitant weak diffraction efficiency. Nevertheless, these experiments successfully demonstrate the concept. The objective of our continuing work in this area is to increase the efficiency for writing the holographic image by amplifying the change in refraction with a polymer dispersed liquid crystalline medium.

(III) LIST OF PUBLICATIONS RESULTING FROM THE PRIOR AWARD

1. Photoisomerization of 2,2"-Ethano-Bridged *m*-Terphenyl Derivatives: Ring Constraint Activates an Unreactive Chromophore. Udayakumar, B. S.; Schuster, G. B. *J. Org. Chem.* **1992**, *57*, 348.

2. Photoracemization of Optically Active 1,1'-Binaphthyl Derivatives: Light-Initiated Conversion of a Cholesteric to Compensated Nematic Liquid Crystal. Zhang, M.; Schuster, G. B. *J. Phys. Chem.* **1992**, *96*, 3063.

3. Photochemistry of Axially Chiral (Arylmethylene)cycloalkanes: A Search for Suitable Photoswitchable Liquid Crystalline Materials. Lemieux, R. P.; Schuster, G. B. *J. Org. Chem.* ***1993*** *58*, 100.

4. Spectroscopic Studies of the Singlet and Triplet Excited States of Some Substituted Biphenylenes. Suarez, M.; Devadoss, C.; Schuster, G. B. *J. Phys. Chem.* ***1993***, *97*, 9299.

5. Photoisomerization of Arylethylenes: Exploring the Singlet Potential Energy Surface of a Partially Planar, Specially Stabilized Compound. Udayakumar, B. S.; Devadoss, C.; Schuster, G. B. *J. Phys. Chem.* **1993**, *97*, 8713.

6. 1-Benzylidene-2,3:4,5:6,7-tribenzocyclohepta-2,4,6-trienes: Synthesis and Photochemistry of a Series of Optically Active Potential Triggers for Physical Amplification of a Photoresponse in Liquid Crystalline Media. Udayakumar, B. S.; Schuster, G. B. *J. Org. Chem.* **1993**, *58*, 4165.

7. A Search for Photoresolvable Mesogens: Synthesis and Properties of a Series of Liquid Crystalline, Axially Chiral 1-Benzylidene-4-[*p*-(alkyl)]phenylethynyl]phenylcyclohexanes. Zhang, Y.; Schuster, G. B. *J. Org. Chem.* **1994**, *59*, xxxx.

8. Holographic Storage in a Near-IR Sensitive Photochromic Dye, Tarkka, R. M.; Talbot, M.; Brady, D.; Schuster, G. B. *Optics Commun.* **1994**, *24*, xxxx.

(IV) Contribution to the Development of Human Resources in Science

1. **Undergraduate Student Participants**

   (A) Mr. Justin Gallivan, "*Investigation of Discotic Liquid Crystals'*". Presently a senior in chemistry at the University of Illinois. He will attend graduate school in chemistry at MIT or Cal Tech.

   (B) Mr. Scott Reeves, "*Reversible Photodestruction of a Chiral Fulgide*". Presently a junior in chemistry at the University of Illinois. His future plans are uncertain.

2. **Graduate Student Participants**

   (A) Ms. Jennifer Galvin, "*Investigation of Tethered Spiropyrans as Command Layers for Homeotropic, Cholesteric Liquid Crystals*". Presently in the third year of the Ph.D. program in chemistry at the University of Illinois.

   (B) Mr. S. Janicki, "*Reversible Photodestruction of a Chiral Fulgide*". Presently in the second year of the Ph.D. program in chemistry at the University of Illinois.

   (C) Mr. Mauricio Suarez, "*Development of a Chiroptical Switch for Liquid Crystals*". Presently in the third year of the Ph.D. program in chemistry at the University of Illinois.

   (D). Mr. M. Zhang, "*Development of a Chrirochromic Switch for Liquid Crystals*". Presently in the fourth year of the Ph.D. program in chemistry at the University of Illinois.

   (E) Mr. Y. Zhang, "*Development of a Chiroptical Switch for Liquid Crystals*". Presently in the third year of the Ph.D. program in chemistry at the University of Illinois.

3. **Postdoctoral Student Participants**

   (A) Dr. Robert Lemieux, "*Development of a Chiroptical Switch for Liquid Crystals*". Presently an Assistant Professor of Chemistry, Queen's University.

   (B) Dr. B. S. Udayakumar, "*Development of a Chiroptical Switch for Liquid Crystals*", Presently employed by *Tritronix, Inc.,* Chicago, IL.

   (C) Dr. Richard Tarkka, "*IR-Addressable Polymer Dispersed Liquid Crystals for Holographic Images*" (Jointly with Professor D. Brady). Presently at the University of Illinois.